Ions at the air-water interface: An end to one hundred year old mystery?

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Availability of highly reactive halogen ions at the surface of aerosols has tremendous implications for the atmospheric chemistry. Yet neither simulations, experiments, nor existing theories are able to provide a fully consistent description of the electrolyte-air interface. In this paper a new theory is proposed which allows us to explicitly calculate the ionic density profiles, the surface tension, and the electrostatic potential difference across the solution-air interface. Predictions of the theory are compared to experiments and are found to be in excellent agreement. The theory also sheds new light on one of the oldest puzzles of physical chemistry — the Hofmeister effect.

Since van't Hoff's experimental measurements of osmotic pressure more than 120 years ago, electrolyte solutions have fascinated physicists, chemists, and biologists alike [1]. The theory of Debye and Hückel (DH) [2] was able to address almost all of the properties of bulk electrolytes. On the other hand, electrolyte-air interface remains a puzzle up to now. The mystery appeared when Heydweiller [3] measured the surface tension of various electrolyte solutions and observed that it was larger than the interfacial tension of pure water. While the dependence on the type of cation was weak, a strong variation of the excess surface tension was found with the type of anion. The sequence was reverse of the famous Hofmeister series [4], which was known to govern stability of protein solutions against salting-out. An explanation for this behavior was advanced by Wagner [5] and Onsager and Samaras [6] (WOS), who argued that when ions approach the dielectric air-water interface, they see their image charge and are repelled from it. This produces a depletion zone which, with the help of thermodynamics, can be related to the excess surface tension. The theory and its future modifications [7], however, were unable to account for the Hofmeister series and showed strong deviations from the experimental measurements above 100mM concentrations. The fact that something was seriously wrong with the WOS approach was already clear in 1924, when Frumkin measured the potential difference across the air-water interface and found that for all halogen salts — except for fluoride — the electrostatic potential difference (air − water) was more negative for solution than for pure water [8]. This suggested that anions were able to approach the interface closer than the cations, or even be adsorbed to it! This contradicted the very foundation of the WOS theory. The confused state of affairs continued for the next 70 years, until the photoelectron emission experiments [9, 10, 11] and the polarizable force fields simulations [12] showed that Frumkin was right, and ions might be present at the interface. The situation, how-ever, remains far from resolved. Simulations predict so much adsorption that the excess surface tension of NaI solution becomes negative, contrary to experiments [13]. Furthermore, while the electron spectroscopy was finding the surface composition of solution to be enhanced in anions [10], vibrational sum-frequency spectroscopy (VSFS) indicated a significantly diminished anion population in the topmost layer [14]. The two results *appear* to be contradictory. The questions, therefore, remain: Are there ions at the air-water interface? If so, why are they there and what are their concentrations? Besides its relation to the Hofmeister series, availability of highly reactive halogens at the surface of aerosol particles has a tremendous implication for the atmospheric chemistry and might help to explain the excessive rate of ozone depletion observed experimentally [15]. In this Letter a theory will be presented which allows all the pieces of this hundred year old puzzle to fit together.

We begin by studying the excess surface tension γ of an electrolyte solution. This can be calculated by integrating the Gibbs adsorption isotherm equation, $d\gamma = -\Gamma_+ d\mu_+ - \Gamma_- d\mu_-$, where $\Gamma_\pm$ are the ion excess per unit area, and $\mu_\pm$ are the ionic chemical potentials. Suppose that the electrolyte is confined to a mesoscopic drop of water of radius R, corresponding to the position of the Gibbs dividing surface (GDS) [16]. Adsorptions are defined as

$$\Gamma_\pm \equiv \frac{1}{4\pi R^2}\left[\int_0^\infty \rho_\pm(r)4\pi r^2 dr - \frac{4\pi R^3}{3}c_b\right], \quad (1)$$

where $\rho_\pm(r)$ are the ionic density profiles and $c_b = \rho_+(0) = \rho_-(0)$ is the bulk concentration of electrolyte. If the system — water+vapor — contains N ion pairs, Eq. (1) simplifies to $\Gamma\pm = N/4\pi R^2 - c_b R/3$.

Let us first consider the alkali metal cations such as Li^+, Na^+, and K^+. These ions are small and strongly hydrated. They can, therefore, be modeled as rigid spheres of *hydrated* radius a_h and fixed charge q located at the

center. Water and air will be treated as uniform dielectrics of permittivities $\epsilon_w = 80$ and $\epsilon_a = 1$, respectively, with a discontinuity across the GDS. For a cation to move across the GDS, requires shedding its hydration sheath. For small, highly hydrated cations, this costs a lot of energy, resulting in a high potential energy barrier and a strong hardcore-like repulsion from the GDS.

Suppose that a cation is located at position $\mathbf{r_p}$ from the center of the drop. The electrostatic potential inside the electrolyte satisfies the usual DH equation, $\nabla^2\varphi - \kappa^2\varphi = -\frac{4\pi q}{\epsilon_w}\delta(\mathbf{r} - \mathbf{r_p})$, where $\kappa = \sqrt{8\pi q^2 c_b/\epsilon_w k_B T}$ is the inverse Debye length. In the vapor phase the electrostatic potential satisfies the Laplace equation, $\nabla^2\varphi = 0$. For mesoscopic water drops of radius $R \gg 1/\kappa$, curvature can be neglected and the two partial differential equations can be solved using the Hankel transform [17]. Once the electrostatic potential is known, the work required to bring an ion from the bulk electrolyte to some distance z from the interface — z axis is oriented into the drop, with the GDS at $z = 0$ — can be calculated using the Güntelberg charging process [18]. We find,

$$W(z; a_h) = \qquad\qquad\qquad\qquad (2)$$
$$\frac{q^2}{2\epsilon_w} \int_0^\infty dk e^{-2s(z-a_h)} \frac{k[s\cosh(ka_h) - k\sinh(ka_h)]}{s[s\cosh(ka_h) + k\sinh(ka_h)]},$$

where $s = \sqrt{\kappa^2 + k^2}$. Eq. (2) accounts for two fundamental contributions: the interaction of an ion with its image across the interface, and for the loss of screening resulting from breaking of spherical symmetry near the surface. In their theory of surface tension, Onsager and Samaras included ionic size by adopting the bulk spherically symmetrical potential of Debye and Hückel. By doing this, they have failed to account for the loss of screening near the interface, which leads to additional repulsion. This is one of the reasons why WOS theory significantly underestimates surface tensions of "hard" non-polarizable electrolytes such as NaF [17].

While the alkali metal ions are strongly hydrated, the large halogen anions, such as iodine and bromide, have low electronic charge density and are weakly hydrated. To solvate an ion of radius a_0, requires creation of a cavity and disturbance of the hydrogen bond network. For small cavities of radius $a_0 < 4$ Å, the free energy cost scales with the volume of the void [19]. If part of the ion leaves the aqueous environment, the cavitational energy will decrease proportionately to the volume exposed. This results in a short range cavitation potential which forces ions to move across the air-water interface,

$$U_{cav}(z) = \begin{cases} \nu a_0^3 \, ; z \geq a_0 \\ \frac{1}{4}\nu a_0^3 \left(\frac{z}{a_0} + 1\right)^2 \left(2 - \frac{z}{a_0}\right) ; -a_0 < z < a_0. \end{cases} \quad (3)$$

From bulk simulations [20], we obtain $\nu \approx 0.3 k_B T/\text{Å}^3$. For strongly hydrated alkali metal cations, the cavitational energy cost is too low to compensate the loss of

hydration and the exposure of ionic charge to the low dielectric environment. For soft, unhydrated halogens, the situation is very different. As these ions move across the interface, they progressively shift their charge towards the part that remains hydrated, thus allowing them to reduce the cavitational energy at a small price in electrostatic self energy [21].

To see how this works, consider a perfectly polarizable ion modeled as a conducting spherical shell of radius a_0 and charge q, free to distribute itself over its surface. The electrostatic self energy [21] of such an ion when its center is located at distance z from the GDS is $U_s(z) = \frac{q^2}{2\epsilon_w a_0} \frac{1}{\frac{\arccos(z/a_0)}{\pi} + \frac{\epsilon_a}{2\epsilon_w}}$. This expression is accurate for $-a_0 < z < a_0/4$, and is exact for ions located precisely at the GDS, $z = 0$. For such ions, $U_s(0) \approx q^2/\epsilon_w a_0$, which is more than an order of magnitude lower than the electrostatic energy of a hard non-polarizable ion at the same position, $\sim q^2/4\epsilon_a a_0$!

Although fundamentally important at the interface, for distances $z \geq a_0$, effects of ionic polarizability are negligible. This can be verified by noting that for a hard ion located at $z = a_0$, the electrostatic self energy is $U_{hard}(a_0) = 3q^2/4\epsilon_w a_0$. On the other hand, the self energy of a perfectly polarizable ion at the same position is $U_{soft}(a_0) = q^2/2\ln(2)\epsilon_w a_0$, which can be calculated exactly by resumming a series of images necessary to keep the ion at fixed potential. For $a_0 \approx 2$Å, the difference between $U_{hard}(a_0)$ and $U_{soft}(a_0)$ is about $0.1 k_B T$. Therefore, for distances $z > a_0$, the ionic polarizability can be neglected. The above calculation was performed in the infinite dilution limit. At finite ionic concentrations, polarization effects will be even less significant, since all the induced interactions are doubly screened [22]. For $z > a_0$ the anion-interface electrostatic potential will, therefore, be well approximated by Eq. (2), with $a_h \to a_0$. The total anion potential can then be obtained by interpolating between Eq. (2) and $U_s(z)$. We find

$$U_{tot}(z) = \begin{cases} W(z; a_0) + \nu a_0^3 + \frac{q^2}{2\epsilon_w a_0} & \text{for } z \geq a_0 \\ \frac{W(a_0; a_0)z}{a_0} + U_s(z) + U_{cav}(z) & \text{for } 0 < z < a_0 \\ U_s(z) + U_{cav}(z) & \text{for } -a_0 < z \leq 0 \end{cases} \quad (4)$$

Since the electrostatic self energy is extremely large for $z < -a_0$, no ion will be found at these distances.

So far our discussion has been for perfectly polarizable ions. Real ions, however, have finite polarizability. The polarization potential for such ions has been derived in reference [21]. For such ions, Eq. (4) should be modified by replacing the ideal potential $U_s(z)$, by the polarization potential $U_p(z)$ of reference [21]. The potentials of all ions are plotted in Fig. 1.

The ionic density profiles can now be calculated numerically by solving the non-linear modified Poisson-Boltzmann equation (mPB) $\nabla^2\phi(r) =$
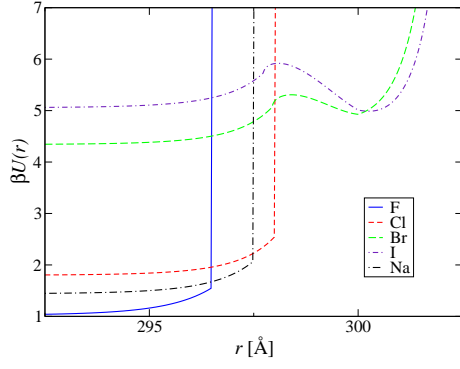
FIG. 1: The ion-surface interaction potentials at 1M salt concentration. For hydrated ions there is a hardcore repulsion from the GDS located at $r = 300$Å, and the cavitational energy is omitted since it is constant.

$-\frac{4\pi q}{\epsilon_w} \left[\rho_+(r) - \rho_-(r) \right]$, where

$$\rho_-(r) = \frac{Ne^{\beta q\phi(r) - \beta U_{tot}(r)}}{\int_0^{R+a_0} 4\pi r^2 \, dr \, e^{\beta q\phi(r) - \beta U_{tot}(r)}} \quad (5)$$

$$\rho_+(r) = \frac{N\Theta(R - a_h - r)e^{-\beta q\phi(r) - \beta W(z; a_h)}}{\int_0^{R-a_h} 4\pi r^2 \, dr \, e^{-\beta q\phi(r) - \beta W(z; a_h)}} \ ,$$

and Θ is the Heaviside step function. The excess surface tension of electrolyte solution can then be obtained by integrating the Gibbs adsorption isotherm equation (1) with $\beta\mu_\pm = \ln(c_b\Lambda_\pm^3)$, where $\Lambda_\pm$ is the de Broglie thermal wavelength.

We start with NaI. Since I^- is large and soft, it should be unhydrated in the interfacial region. For its radius, we use the value calculated by Latimer, Pitzer, and Slansky [23] from fitting the experimentally measured free energy of hydration to the Born model. Latimer radii for halogens come out to be almost identical to the Pauling crystal radii, differing from them by only 0.1 Å. Since in the bulk our theory reduces to the Born model, Latimer radii: $a_I = 2.26$ Å, $a_{Br} = 2.05$ Å, $a_{Cl} = 1.91$ Å, and $a_F = 1.46$ Å, are particularly appropriate. For ionic polarizabilities we will use the values from reference [24]: $\gamma_I = 7.4$ Å^3, $\gamma_{Br} = 5.07$ Å^3, $\gamma_{Cl} = 3.77$ Å^3, and $\gamma_F = 1.31$ Å^3. Our strategy will be to adjust the hydrated radius of Na^+ to best fit the experimental surface tension for NaI. The same value of a_h, will then be used to calculate the surface tension of other sodium salts and compare them to the experimental measurements [25]. Fig. 2 shows the result of this procedure. We find that $a_h = 2.5$ Å gives an excellent fit to the experimental data for NaI. Since Br^- ion is also large and soft, we expect that it will also remain unhydrated in the interfacial region. This expectation is well justified, and a good agreement is obtained with the experimental data, Fig. 2. The situation should be very different for F^-, which is small, hard, and strongly hydrated. This means that just
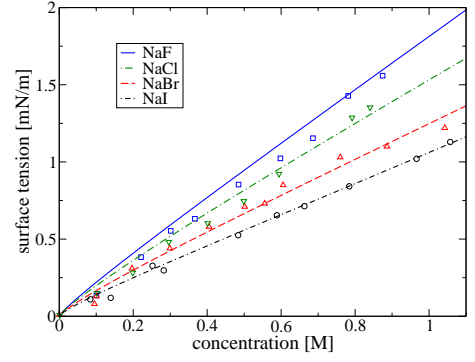

FIG. 2: Surface tension of NaF, NaCl, NaBr, and NaI. Na^+ and Cl^- are partially hydrated with $a_h = 2.5$ Å and 2.0 Å, respectively, F^- is fully hydrated with $a_h = 3.52$ Å, while the large halogens I^- and Br^- are unhydrated. Symbols are the experimental data from [25].
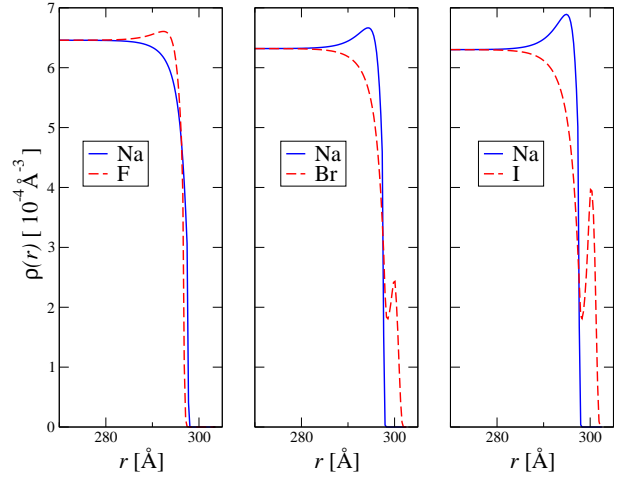

FIG. 3: Density profiles for NaF, NaBr, and NaI at 1M concentration. The GDS is at $r = 300$Å.

like for cation, a hard core repulsion from the GDS must be explicitly included in the mPB equation. We then find an almost perfect agreement with the experimental data using the bulk hydrated radius of F^-, $a_h = 3.52$ Å [26]. The most difficult electrolyte to study theoretically is the usual table salt, NaCl. The size of chloride is sufficiently small that hydration must be taken into account. At the same time, it is also quite polarizable. We find that using Latimer size for Cl^- gives a very reasonable agreement with experiment, however, the agreement can be made perfect if we assume a small hydration, $a_h = 2.0$ Å.

The density profiles for NaF, NaBr, and NaI are shown in Fig.3. In agreement with the polarizable force fields simulations, the density profiles for large halogens I^- and Br^- differ significantly from the classical WOS picture. We find that there is a considerable concentration of anions at the GDS. However, unlike simulations [13], and in

agreement with the surface tension experiments, our adsorption always remains negative. The theory also agrees with the electron spectroscopy measurements showing that close to the GDS, there is a larger excess of anions *over* cations. However, just as was found using VSFS, the absolute concentration of anions at the surface is about half that of the bulk. We are, therefore, able to reconcile the two sets of *apparently* contradictory experimental results. Finally, we calculate the excess electrostatic potential difference across the interface, $\Delta\chi$, for 1M solutions of NaF, NaCl, NaBr, and NaI . We obtain: $+3.8$, -1.9, -9.1, and -14.0 mV, for the four salts respectively. These are quite close to the values originally measured by Frumkin [8, 27]. In particular, one should note the change of sign of the electrostatic potential going from NaF to NaCl, first observed by Frumkin and confirmed by the present theory.

We have seen that by adjusting *only* the hydrated radius of sodium cation, we are able to account for the surface tensions of four different electrolyte solutions and for their values of $\Delta\chi$. It should, therefore, be possible to predict the surface tensions and the $\Delta\chi$ of other salts — as long as their anions are sufficiently large and weakly hydrated. This is the case, for example, for $NaNO_3$, $NaIO_3$, and $NaClO_4$. The only experimental data available to us is for $NaNO_3$ [28] which, once again, shows a good agreement between the theory and experiment. For $NaClO_4$, we find that at low concentrations the excess surface tension is very small (slightly negative) but grows with increasing concentration of electrolyte. For 1M $NaClO_4$, the calculated value of $\Delta\chi$ is -42 mV, while the value originally measured by Frumkin was -48 mV [27]. For 1M $NaNO_3$ and $NaIO_3$, we obtain $\Delta\chi = -8.2$ and -22 mV, respectively.

We have presented a theory which allows us to calculate surface tensions and surface potentials for seven different electrolyte solution using only *one* adjustable parameter — the hydrated radius of sodium cation, $a_h = 2.5$ Å. This value is very reasonable, lying between the Pauling crystal radius and the bulk hydration radius of Na^+. In the case of five sodium salts for which there is experimental data available to us, the theory is found to be in very good agreement with the measured surface tensions. Using the *same* value of a_h, we are also able to account for the experimentally measured electrostatic potential differences across the solution-air interfaces. The theory provides a very interesting picture of the interfacial region: alkali metal cations and fluoride anion are strongly hydrated and are repelled from the GDS. On the other hand, heavy halogens, Br^- and I^-, and the monovalent oxy-anions, NO_3^-, IO_3^-, and ClO_4^-, are unhydrated, and as a result of their polarizability are significantly adsorbed to the surface. Nevertheless, their absolute concentration at the GDS remains below that of the bulk value. All these conclusions are in agreement with recent photoelectron spectroscopy and the VSFS measurements. In view of the success of the theory, it seems reasonable to hope that a fully quantitative understanding of the Hofmeister effect might now be in sight.

[1] Y. Levin, Rep. Prog. Phys. **65**, 1577 (2002).
[2] P. W. Debye and E. Hückel, Phys. Z. **24**, 185 (1923).
[3] A. Heydweiller, Ann. Physik **33**, 145 (1910).
[4] F. Hofmeister, Arch. Exp. Pathol. Pharmakol. **24**, 247 (1888); W. Kunz, P. Lo Nostro, and B. W. Ninham, Curr. Op. Colloid Interf. Sci. **9**, 1 (2004).
[5] C. Wagner, Phys. Z. **25**, 474 (1924).
[6] L. Onsager and N. N. T. Samaras, J. Chem. Phys. **2**, 528 (1934).
[7] A. L. Nichols III and L. R. Pratt, J. Chem. Phys. **80**, 6225 (1984). Y. Levin, J. Chem. Phys. **113**, 9722 (2000); H. Ohshima and H. Matsubara, Colloid and Polymer Sci. **282**, 1044 (2004); D. S. Dean and R. R. Horgan, Phys. Rev. E **69**, 061603 (2004); A. Onuki, J. Chem. Phys. **128**, 224704 (2008); M. Bier, J. Zwanikken, and R. van Roij, Phys. Rev. Lett. **101**, 046104 (2008).
[8] A. Frumkin, Z. Physik. Chem. **109**, 34 (1924).
[9] G. Markovich, S. Pollack, R. Giniger, and O. Cheshnovsky, J. Chem. Phys. **95**, 9416 (1991).
[10] S. Ghosal and et al., Science **307**, 563 (2005).
[11] B. Garrett, Science **303**, 1146 (2004).
[12] L. Perera and M. L. Berkowitz, J. Chem. Phys. **95**, 1954 (1991); L. X. Dang and D. E. Smith, J. Chem. Phys. **99**, 6950 (1993); S. J. Stuart and B. J. Berne, J. Phys. Chem. A **103**, 10300 (1999); P. Jungwirth and D. J. Tobias, J. Phys. Chem. B **106**, 6361 (2002); P. Jungwirth and D. J. Tobias, Chem. Rev. **106**, 1259 (2006); D. Horinek and R. R. Netz, Phys. Rev. Lett. **99**, 226104 (2007); M. A. Brown and et al., Phys. Chem. Chem. Phys. **10**, 4778 (2008).
[13] T. Ishiyama and A. Morita, J. Phys. Chem. C **111**, 721 (2007).
[14] E. A. Raymond and G. L. Richmond, J. Phys. Chem. B **108**, 5051 (2004).
[15] E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. Dabdub, and B. J. Finlayson-Pitts, Science **288**, 301 (2000).
[16] C.-H. Ho, H.-K. Tsao, and Y.-J. Sheng, J. Chem. Phys. **119**, 2369 (2003).
[17] Y. Levin and J. E. Flores-Mena, Europhys. Lett. **56**, 187 (2001).
[18] E. Z. Guntelberg, Z. Phys. Chem. **123**, 199 (1926).
[19] K. Lum, D. Chandler, and J. D. Weeks, J. Phys. Chem. B **103**, 4570 (1999).
[20] S. Rajamani, T. M. Truskett, and S. Garde, PNAS **102**, 9475 (2005).
[21] Y. Levin, Phys. Rev. Lett **102**, 147803 (2009).
[22] M. E. Fisher, Y. Levin, and X.-J. Li, J. Chem. Phys. **101**, 2273 (1994).
[23] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, J. Chem. Phys. **7**, 108 (1938).

[24] N. C. Pyper, C. G. Pike, and P. P. Edwards, Molecular Phys. **76**, 353 (1992).

[25] N. Matubayasi, K. Tsunemoto, I. Sato, R. Akizuki, T. Morishita, A. Matuzawa, and Y. Natsukari, J. Colloid and Interface Sci. **243**, 444 (2001).

[26] E. R. Nightingale Jr., J. Phys. Chem. **63**, 1381 (1959).

[27] J. E. B. Randles, *Advances in Electrochemistry and Electrochemical Engineering* (Interscience, New York, 1963), vol. 3, p. 1.

[28] N. Matubayasi and R. Yoshikawa, J. Colloid and Inter. Sci. **315**, 597 (2007).